Electronic structure determined from α- and ε- Fe₂O₃ nanoparticles

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Hematite (α-Fe₂O₃) is commonly used as photocathode for water splitting for the hydrogen production /1/. Epsilon is fascinating because of its magnetic properties /2/. As reference systems with well defined structural properties we report on spectroscopic investigations on nanoparticles of α- and ε- Fe₂O₃ /3,4/. We focus on the detailed analysis of the O1s resonance profile by resonant photoelectron spectroscopy /5/. We analyze the electronic structure and assign the O2p to build the valence band and both, O2p and Fe4s states to contribute to the conduction band. We determine the partial density of states for the valence and conduction bands and find a strong hybridization of O2p and Fe4s states. This is deduced from constant final state spectra on the O K-edge and Fe L2,3-edge and a comparison to the corresponding X-ray absorption spectroscopy data. We also identify several types of intrinsic defects which cause electronic states within the band gap. A broad band of oxygen derived defects is identified that extends throughout the gap. Small polarons are attributed to cause an anti-resonance in the valence states around the O1s threshold. In addition, a separate Auger decay at resonance indicates the existence of localized charge transfer states which involves localized Fe3d states.


Figure 1. Combined partial density of states for the valence band and the conduction band determined by XPS and XAS measurements. All energies are referred to Fermi level (E_F). The dashed lines mark valence band maximum (VBM), conduction band minimum (CBM) and E_F.